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Study of innovative chemical processes for sodium fast reactor fuel assemblies cleaning

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Abstract

Within the framework of Sodium Fast Reactor, innovative solutions for fuel assemblies cleaning are investigated. This process consists in removing residual sodium to avoid water pollution and hydrogen production in water storage. It takes place before head operations of cooling and reprocessing. An innovative process that is currently tried out consists in the addition of mineral salts in the cleaning water.
First, the process will be described from a theoretical point of view, then the experimental device, that enables the measurement of the impact of different mineral salts on the kinetics via pressure measurements or hydrogen analysis, will be presented.

Keywords: Cleaning; Sodium; Water; Electrolytes; Sodium Fast Reactor; Head operations

1. Introduction

Within the framework of Sodium Fast Reactor (SFR) development, innovative solutions to enhance safety, competitiveness and availability of future reactors are investigated. The matter of irradiated fuel handling takes place in particular in the reactors availability aspects. The cleaning process is an essential first step before the head operations of cooling and reprocessing. When a fuel assembly is removed from the primary reactor vessel,

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the cleaning of residual sodium is necessary before water storage for cooling [1]. This process is currently based on a controlled Sodium Water Reaction (SWR):

$Na + H_2O \rightarrow NaOH + H_2$

The latter is very exothermic; it produces 180 kJ/mol Na, quasi instantaneously. It also generates chemical compounds: hydrogen and caustic soda. Hydrogen is a highly flammable gas (Lower Flammability Limit: 4% in H_2-air mixture, room temperature). Sodium Hydroxide may induce corrosion of clad assemblies.

During the operations of cleaning French SUPERPHENIX SFR Reactor fuel assemblies, most of them are washed with the help of the carbonation process. It consists in the reaction between sodium and a mixture of water mist and carbon dioxide flow injected through the fuel assembly. Carbon dioxide reacts with soda issued from SWR reaction. Carbonation avoids corrosion, carbonate products are rinsed out with water. However, this process is not totally powerful with all kind of assemblies due to their geometry, for example with sodium retention. For those which this technique is not effective, a cleaning process using water without additive is employed. In order to eliminate problems due to the kinetics of the SWR, assemblies are immersed slowly in water in cleaning pits. Immersion velocity is maintained between 2 cm/min and 10 cm/min. This leads to a very long cleaning duration of about 8 hours.

The challenging performances of the new SFR fuel assembly cleaning require to respect several criteria:
- a simplification of the process,
- an improvement of safety,
- a decrease of the duration of the operations,
- a greater flexibility allowing to treat any type of fuel assembly.

To achieve this, some R&D studies are currently conducted at the CEA Cadarache.

This paper deals with the first results obtained with a new cleaning process using aqueous solutions of mineral salts and with the new experimental device dedicated to these studies. In a first part, the characteristics of the SWR and ways of investigation to mitigate it are presented. Then, the experimental set-up is described.

2. Improvement of mitigation for SWR use

2.1. Innovative way

The objective of this study is the slowdown of the kinetics rate of the reaction between sodium and water.

Therefore, a first way would be to add one of the products of the reaction in the solution as aqueous sodium hydroxide.

Thus sodium hydroxide solution has already been used in order to clean, under safe conditions, elements which had been polluted with sodium. This process, called NOAH [2], uses a 10 mol/L NaOH aqueous solution. Its goal consists in the destruction of large quantities of sodium without the violence of the SWR. But the presence of caustic soda associated with a high temperature may induce crack corrosion.

To mitigate corrosion, the use of alternative mineral salts was suggested.

Some minerals salts, added in the cleaning aqueous solution, were tested at CEA Cadarache in order to evaluate their qualitative influence on the cleaning rate [3].

The first experiments were carried out with four sodium salts: sodium chloride (NaCl), sodium iodide (NaI), sodium phosphate (Na_3PO_4, $12H_2O$) and sodium nitrate ($NaNO_3$). These salts were selected according to the following criteria:

- high solubility in order to avoid plugging of washed components,
- availability,
- cost.

The tests were performed in a cell dedicated to hydrolysis of sodium studies, at room temperature. A sample of massive sodium (no more than 2 grams) was immersed in a solution under argon (to prevent presence of oxygen and flammability risk). The temperature of the solution was measured by a thermocouple, the solution was not agitated. Salt concentrations from 2.5 to 10 M were selected except in the case of sodium phosphate because of its low solubility. The latest concentration is between 0.2 and 0.5 M.

Sodium chloride and sodium iodide are interesting for their solubility despite their material corrosion drawbacks. Furthermore their solutions are neutral. Sodium nitrate exhibits a high solubility. Sodium phosphate is quite soluble and has detergent properties though it has environmental issues related to a difficult and expensive effluents reprocessing.

The experiments were carried out with the salts alone or mixed with soda.

Nitrate salts induce a violent reaction; other tested salts seem to show moderation during the SWR. However, in sodium chloride and sodium iodide solutions, sodium fragmentation disturbed the experiments.

Other salt studies on the moderation of SWR were performed by A.R. Lakshmanan et al. [4]. They found that the reaction of sodium with water-insoluble salts is not feasible, leading for example to sodium fire (case of gypsum ($CaSO_4 \cdot 2H_2O$)). $(NH_4)_2SO_4$ aqueous solutions react with sodium efficiently, but the production of ammonia is incompatible as it is known to react violently with sodium. Many other salts were studied. For example, sodium chloride and potassium chloride exhibit a non-totally quiet reaction with sodium. The best solution found to eliminate sodium is a concentrated aqueous solution of ($MgSO_4$, 7 H_2O), so-called EPSOM salt. The SWR in presence of this salt is mildly exothermic; the reaction products (mixed salts of $MgSO_4$, Na_2SO_4, insoluble $Mg(OH)_2$) are considered as non-corrosive and non-hazardous. EPSOM salt is also eco-friendly and inexpensive. $MgSO_4$ may be converted to $Mg(OH)_2$ through the following reaction: $2\ NaOH + MgSO_4 \rightarrow Mg(OH)_2 + Na_2SO_4$

According to the authors, the solution was successfully tested with a high pressure sprayed solution.

Another way of research to mitigate the SWR is to eliminate the reaction products, hydrogen and soda, in situ, in view to suppress corrosion and flammability problems. This could be achieved by the use of oxydoreductive reaction [5] thanks to the implementation of particular salts exhibiting redox behaviour. H_2 formed, or more precisely native H formed, by the SWR reaction could react by the way of a redox process, leading to H^+ or H_3O^+. This would assure a neutral pH, due to the subsequent elimination of hydroxide anion. By such a process, both corrosion and hydrogen formation drawbacks could be suppressed.

2.2. Phenomena discussion

The effect of mineral salts on the kinetics of the SWR is currently being studied. Several assumptions are considered: the salt effect may be related to chemical kinetics itself or to physico-chemical phenomena as the SWR is heterogeneous. This study concentrates on chemical kinetic aspects.

The addition of salt in an aqueous solution usually influences the kinetics of the reaction. This has extensively been demonstrated for homogeneous solutions of solutes [6] and may be applied to a heterogeneous reaction such as SWR, which involves water (solvent) and sodium (solid).

The hypothesis is the following: the addition of salts decreases the number of water molecules available for a reaction with sodium, so the rate of the reaction should decrease as well. This can partly been seen as a question of hydration. Then, the hydration number of ions may indicate which mineral salts would most decrease the rate of SWR**Erreur ! Source du renvoi introuvable.** presents some published values of various ions hydration [7].

Table 1. Hydration numbers for some ions [7]

cation	h_i^∞	anion	h_i^∞
Li^+	7.4	Cl^-	3.9
Na^+	6.5	I^-	2.8
K^+	5.1	F^-	5.5
Rb^+	4.7	Br^-	3.4
Cs^+	4.3	CO_3^{2-}	7.1
Ca^{2+}	10.4	SO_4^{2-}	5.3
Cu^{2+}	10.3	MnO_4^-	2.9
Ba^{2+}	9.6		
Fe^{2+}	11.8		
Al^{3+}	16.8		
Fe^{3+}	15.5		

The kinetic rate of a reaction may be expressed in terms of chemical activities of the different components involved in the reaction. So, in the case of SWR, kinetic law could be expressed as a function of water activities which depend on the nature of salts. The water activity can be measured with the help of osmotic coefficients. The water activity, a_w, can be calculated from the osmotic coefficient Φ through the equation:

$$\Phi = - n_w/\nu\, n_s\, ln(a_w)$$

With n_w the number of moles of water, n_s the number of moles of salt and ν the number of ion resulting of the dissociation of the considered salt. All water activities calculated in this paper are based on osmotic coefficients issued from references [8, 9, 10, 11].

Figure 1a reports the water activity as a function of the molality (mol/kg) of the solution in the case of soda and EPSOM salt. A close behaviour is observed in the same range of molality (cf. Figure 1a) with a continuous decreasing water activity with the increasing of molality (without any extremum).

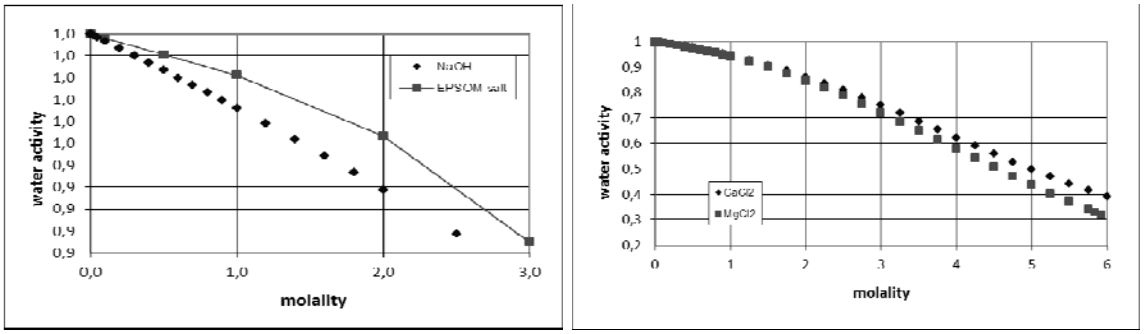

Figure 1. Water activities of some salts vs. molalities. (a) Comparison of NaOH 25°C from [8] / EPSOM salt solutions at 25°C from [9], molality (mol/kg), (b) Comparison of $CaCl_2$ [8] / $MgCl_2$ solutions at 25 °C from [10], molality (mol/kg).

The water activities versus molality of aqueous solutions of calcium chloride and of magnesium chloride are compared in Figure 1b. According to Lakshmanan [4], the aqueous solution of calcium chloride ($CaCl_2$, $2H_2O$) reacts with sodium efficiently (though the drawback of the formation of solid $Ca(OH)_2$). By contrast, magnesium

chloride solution is not efficient. However, though the behaviour of these two solutions with sodium are very different, their activities are close at a given molality.

Then, even if the change of water activity has an effect on the SWR in presence of salts, this effect is not the only one and seems to be not predominant. There must be one or several other effects present in the solution or due to the heterogeneous nature of the reaction that would explain the decrease of the kinetics of the reaction, in some cases. This will be confirmed with experimental results.

What is sure is that the available experimental results are currently not sufficient to conclude. It is necessary to obtain some quantitative data about the kinetics of the reaction in presence of mineral salts and to build an experimental data base. Consequently a new experimental device has to be implemented.

3. Experimental set-up

An experimental set-up, called LAVINO ('LAVages INnOvants': Innovative Cleaning in French), has been designed and is currently set at the CEA Cadarache (see Figure 2). This apparatus will enable to compare the quantitative effects of mineral salts on the kinetics of the SWR. The experiment consists in immersing a piece of sodium or steel plates wetted by sodium in mineral salts aqueous solution.

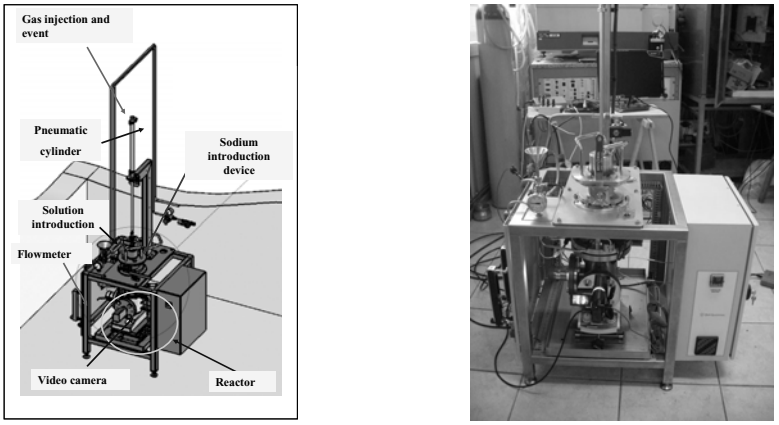

Figure 2. LAVINO experimental device

The reactor is placed at the bottom of the device and is inerted. A magnetic hot plate stirrer heats and mixes the solution to ensure that the solution remains homogeneous during the experiments. A specific sodium introduction device, equipped with a valve, enables to bring sodium from an inert glove box to the reactor and to avoid any contact with air. This prevents the oxidation of the surface of the sample of sodium which would perturb the kinetics. Mass, surface and shape of pieces of sodium are reproducible due to the use of an adapted punch. Sodium is introduced in the reactor and immersed into the solution thanks to a pneumatic cylinder. The equipment is also designed to allow a spray of a salt solution on a wetted sodium plate out of stainless steel. A fast video camera allows the examination of the behaviour of the reagents during the reaction. Inside the reactor, gas and liquid temperatures are measured.

Two types of experiments may be carried out:

- pressure tests in closed and tight reactor to evaluate the dynamic pressure peak due to the SWR reaction, thanks to a dynamic pressure sensor. It aims to determine the influence of the aqueous phase on this pressure peak (influence of salts or of redox conditions),

- gas sweeping tests in which argon is injected into the reactor plenum and a vent enables gas venting. An aliquot of gas is sampled in the vent pipe and lead to analysis by mass spectrometry. A continuous measurement of hydrogen gas enables the analysis of the reaction and gives a direct access of its kinetics.

The first experiments are currently in progress. The following salts, gathered in Figure 3, are to be tested:

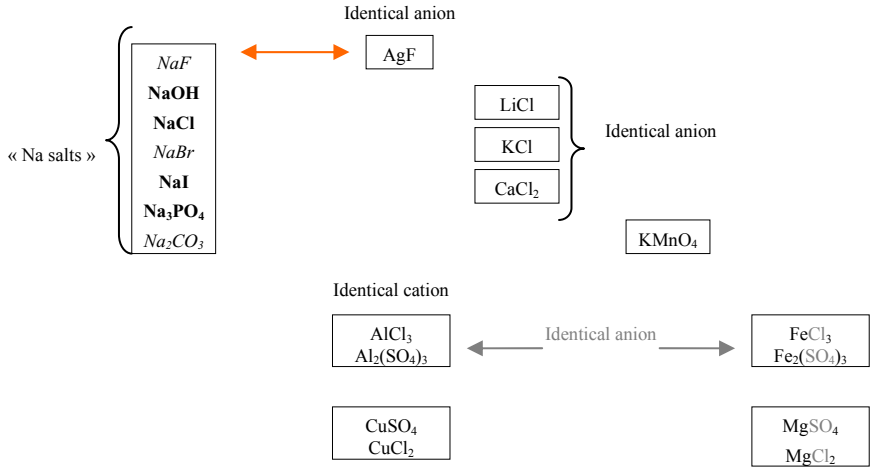

Figure 3. Mineral salts initially consider

The use of various salts with identical cation or anion will permit to compare the effect of each ion. The variation of the anion between salts with an identical cation allows the comparison of the effect of the anions on the kinetics of the reaction. This is why the following salts will be tested: NaF, NaOH, NaCl, NaBr, NaI, Na_3PO_4 and Na_2CO_3. In the same way, the effect of cation will be considered with the help of: AgF, NaF, on one part, and LiCl, KCl, $CaCl_2$, on the other part.

All the mineral salts tested in the LAVINO experimental device are preliminary studied in anhydrous conditions in presence of sodium via calorimetry. This allows to point out potential secondary reactions between the sodium and the mineral salt itself which would disturb the sodium water reaction. Indeed calorimetry easily enables to highlight reactions thanks to their endothermic or exothermic behaviour.

As an example, a comparison of thermograms of different minerals salts in presence of sodium is reported in the Figure 1. Though the results have to be considered cautiously because the medium and the temperature are different from the aqueous situation, they may give some indications on a potential concurrent reaction between sodium and salts. It could be seen that most of the studied salts don't react with sodium. That is consistent with the results previously described for which the corresponding salts allowed a mitigated SWR reaction. By contrast, copper sulfate and above all, sodium nitrate, violently react with sodium. For the latter a similar effect was observed in aqueous solution. Of course, the salt/Na reaction may only occur in aqueous solution if its kinetics is similar to the SWR one.

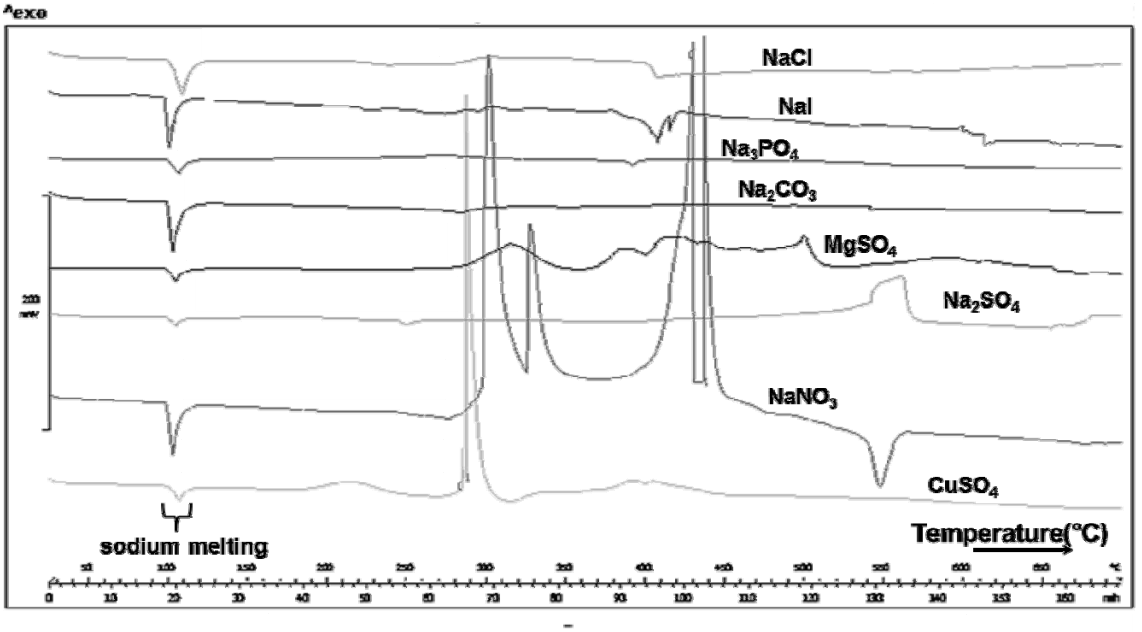

Figure 4. Calorimetric studies of Na/mineral salts systems. Thermograms of different salts with sodium: NaCl(33mg)-Na(35mg), NaI(29mg)-Na(34mg), Na_3PO_4(11mg)-Na(14mg), Na_2CO_3(31mg)-Na(35.4mg), $MgSO_4$(12mg)-Na(12mg), Na_2SO_4(14mg)-Na(8mg), $NaNO_3$(38mg)-Na(33mg), $Cu(SO_4)$ (9mg)-Na(13mg),

First studies were recently conducted in LAVINO device. The first results obtained with NaCl point out a fast reaction, sodium disappears in less than one minute. The apparatus allows to observe the reaction and through the porthole, a photography of can be taken from the video. As we can see on Figure 5, it points out the formation of hydrogen during the reaction between sodium and water in presence of NaCl 3M.

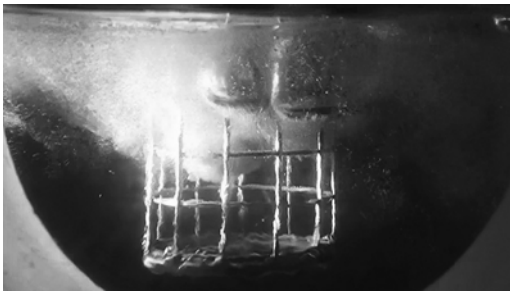

Figure 5. Picture of the SWR in presence of NaCl 3M in LAVINO device at 25°C.

4. Conclusion

In view to limit the kinetics and the reaction products impact on the sodium water reaction used to clean the fuel assemblies of Sodium Fast Reactor (SFR), the addition of different mineral salts are currently experimented. Water molecules hydrate salt ions, therefore are less available for SWR and may induce a slowdown of the

kinetics. Considering the heterogeneous nature of the reaction, it is obvious that other physicochemical phenomena are involved and have to be elucidated.

From an experimental point of view, LAVINO device, whose main characteristics are described in this article, will allow us to obtain an experimental data base, on which a future modeling could be based on.

The influence of mineral salts in the mechanism of the SWR reaction could also be studied by molecular modeling. Many published papers carried out investigations to understand the SWR molecular mechanism. For example the study of the role of the 3s electron of sodium is investigated using molecular dynamics and functional density theory [12, 13]. The introduction of salt ions in such a modeling may lead to a further understanding of the phenomenological aspect of the role of salt in sodium water reaction kinetics.

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